Supplementary Information

Synthesis of Benzoquinone Compounds by a Microdroplet-Accelerated Retro-Diels-Alder Reaction

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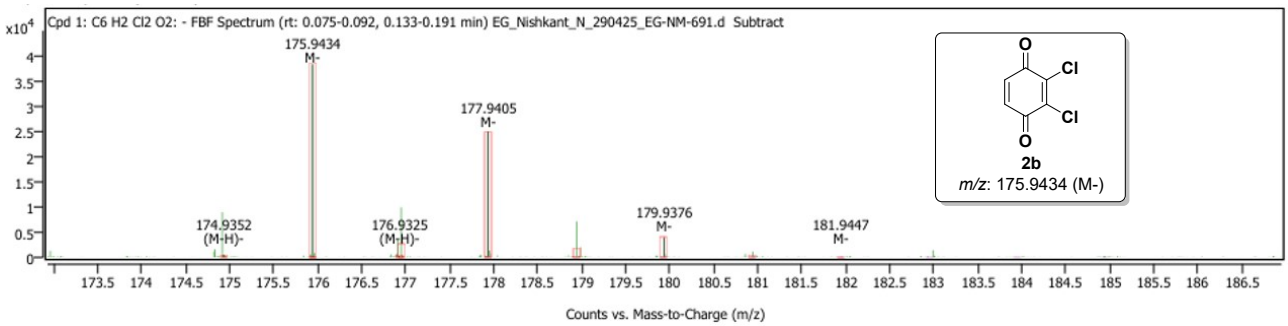
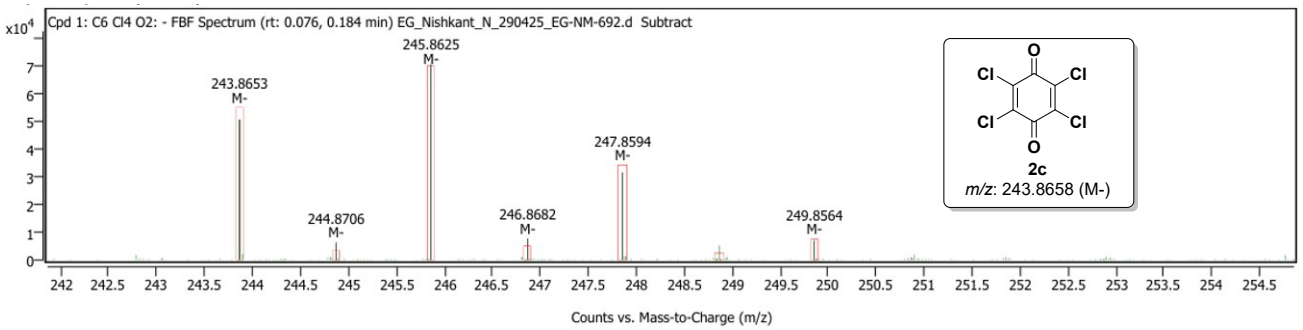
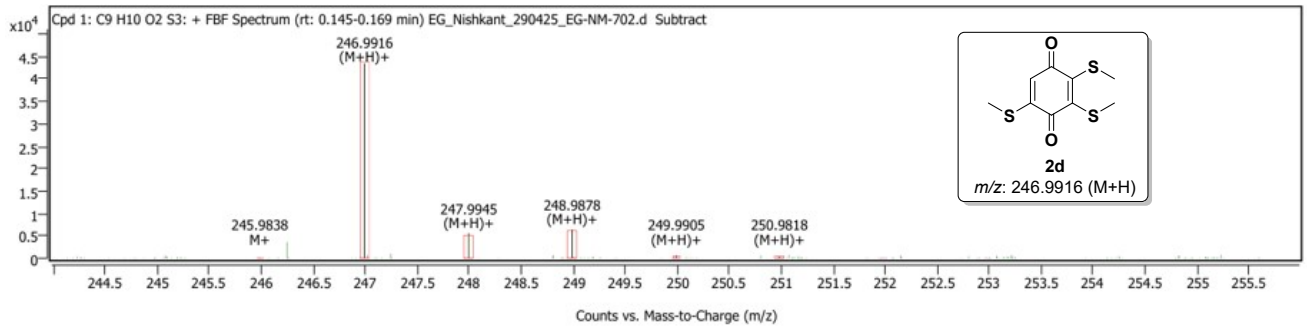
1. General Considerations

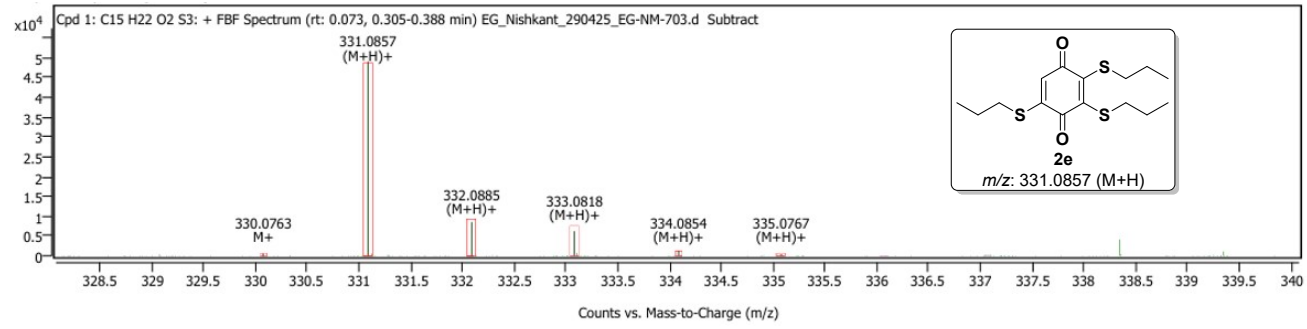
All starting materials were purchased from Hyma Synthesis Pvt. Ltd., India and used without further purification. All the solvents were purchased from Merck, India, and xylenes was purchased from Hyma Synthesis Pvt. Ltd. and used without further purification. Microdroplet spray was used with the fused silica capillary for transfer of solution to the spray source (i.d. of 100 μm and o.d. of 360 μm from Ploymicro Technologies, Az, USA). TLC plate was performed on pre-coated 0.25 mm thick aluminium-backed silica gel plates purchased from Merck KGaA, Germany, and visualized with a UV lamp (λ = 254 nm) or $KMnO_4$–K_2CO_3 in water, followed by heating. Flash chromatography was performed on Merck silica gel (230-400 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on JEOL ECZ500R/S1 instrument. All proton NMR chemical shifts are reported in ppm relative to tetramethylsilane (0.00 ppm) or the residual solvent peak (Chloroform-d δ 7.26 ppm). Multiplets are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. ^{13}C NMR spectra were recorded at 126 MHz, and data are reported as follows: a chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator (Chloroform-d δ 77.16 ppm and DMSO-d6 δ 39.52). HRMS data were obtained in ESI mode by Agilent LC/Q-TOF instrument. All the Diels-Alder adducts were prepared according to reported procedures, and ^{1}H-NMR and ^{13}C-NMR data are consistent with those reported in the literature.

2. Mass spectral data of rDA products (2b -2e):



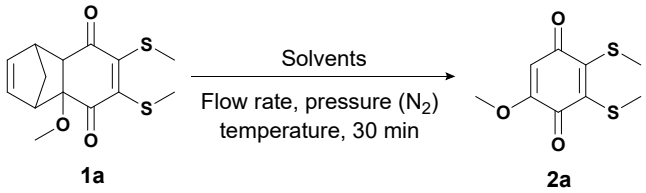






3. Optimisation conditions for rDA reaction:

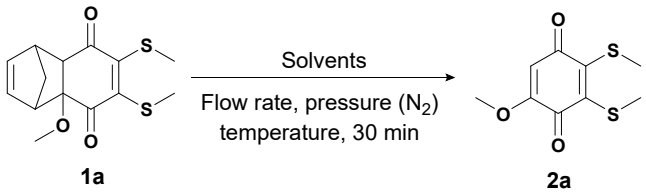
General Procedure I:



1a **2a**

To optimize the reaction condition, the Diels-Alder adduct **1a** was dissolved in various solvents and the solution was loaded into an airtight glass syringe. The solution was delivered with a syringe pump (NE-300, New Era Pump Systems, Inc. Farmingdale, NY, USA) at various flow rates (Table S1) to a fused silica glass capillary (i.d. of 100 μm and o.d. of 360 μm, capillary length: 20 cm). Dry nitrogen, which is served as the sheath gas, was operated at different pressures. The microdroplets were sprayed through a glass tube with varying temperatures, which was equipped with a heating coil (40 mm), and then collected into a 500 ml round-bottom flask. To avoid the thin-film reactions, heat-resistant foam material (10 mm) was kept between the heating coil connected tube and the collection RB flask. The distance between the spray source and the collecting surface was kept at 240 mm. The microdroplets were sprayed for 30 minutes and collected. The collected crude material was then assayed by crude ^{1}H NMR to assess the conversion and purified through flash column chromatography (95:5→80:20, EtOAc/Hexane), which afforded the retro-Diels-Alder product **2a**.

Table S1. Optimization of reaction conditions[a]



1a **2a**

S. No.	Solvent	Pressure (N_2)	Temp. (°C)	Flow rate (µL/min)	Conversion (%)[b]
1	MeOH: Water (1:1)	120 Psi	150	30	0
2	MeOH: Water (1:1)	75 psi	150	30	1
3	Xylenes	120 Psi	150	30	2
4	Xylenes	75 Psi	150	30	3
5	Xylenes	50 psi	150	30	21
6	Xylenes	25 psi	150	30	7
7	Xylenes	50 psi	150	20	30
8	Xylenes	50 psi	150	10	56
9	Xylenes	50 psi	150	5	46
10	Xylenes	50 psi	120	10	13
11	Toluene	50 psi	150	10	41
12	Mesitylene	50 psi	150	10	48
13	ACN	50 psi	150	10	11
14	ACN: H_2O (90:10)	50 psi	150	10	4
15	DMSO: H_2O (90:10)	50 psi	150	10	3
16[c]	Xylenes	50 psi	150	10	18
17[d]	**Xylenes**	**50 psi**	**150**	**10**	**64**
18[e]	Xylenes	50 psi	150	10	55

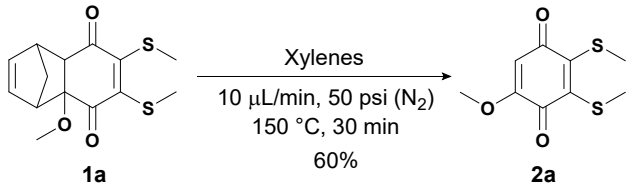
[a]All sprays were performed with 0.042 M concentration of **1a** in solvent. [b]Conversion was determined by crude ^{1}H NMR. [c]Spray was performed with 0.021 M concentration of **1a** in xylenes. [d]Spray was performed with 0.063 M concentration of **1a** in xylenes. [e]Spray was performed with 0.105 M concentration of **1a** in xylenes.

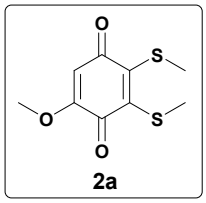
4. Microdroplet synthesis of retro-Diels-Alder product

General procedure II (Substrate scope)

Diels-Alder adduct **1** (0.019 mmol) was dissolved in 0.3 mL of xylenes (0.063 M), and the solution was loaded into an airtight glass syringe. The solution was delivered with a syringe pump (NE-300, New Era Pump Systems, Inc. Farmingdale, NY, USA) at a flow rate of 10 μL/min to a fused silica capillary (i.d. of 100 μm and o.d. of 360 μm, capillary length: 20 cm). The end of the capillary was equipped with a sheath-gas-assisted spray emitter. Dry nitrogen, which served as the sheath gas, was operated at 50 psi. The sprayed volume was subjected to pass through cylindrical flask at 150 ºC, which was equipped with a heating coil (40 mm) into 500 ml round bottom flask. To avoid the thin-film reactions, heat-resistant foam material (10 mm) kept in between the heating coil connected tube and collection RB flask. The distance between the spray source and collecting surface was kept at 240 mm. The solution was sprayed for 30 minutes and collected crude material purified through flash column chromatography, which afforded the corresponding retro-Diels-Alder product **2**.

5-methoxy-2,3-bis(methylthio)cyclohexa-2,5-diene-1,4-dione (2a):





The title compound was prepared according to the general procedure II, using 4a-methoxy-6,7-bis(methylthio)-1,4,4a,8a-tetrahydro-1,4-methano-naphthalene-5,8-dione **1a** (5.6 mg, 0.019 mmol) in xylene (0.3 ml), sprayed for 30 min. The crude product was subjected to flash column chromatography (95:5→80:20, EtOAc/Hexane), afforded the **2a** as a blue solid (2.6 mg, 60% yield). The spectroscopic data are consistent with the reported in the literature.[1]

Physical appearance: blue solid.

Melting Point: 90-92 °C.

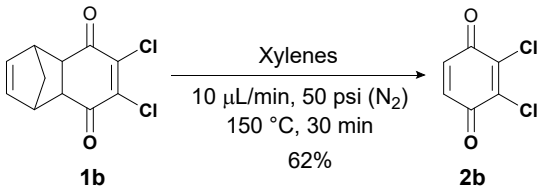
^{1}H NMR (500 MHz $CDCl_3$) δ ppm: 5.88 (s, 1H), 3.81 (s, 3H), 2.69 (s, 3H), 2.58 (s, 3H).

^{13}C NMR (125 MHz $CDCl_3$) δ ppm: 181.2, 175.4, 159.3, 148.2, 140.4, 108.2, 56.7, 18.7, 18.0.

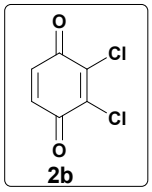
FT-IR (neat): 2922, 2852, 1626, 1498, 1440, 1352, 1289, 1236, 1198, 1046, 962, 857 cm^{-1}.

HRMS: Calculated for $C_9H_{11}O_3S_2^+$ [M+H$^+$] 231.0144, found 231.0149.

2,3-dichlorocyclohexa-2,5-diene-1,4-dione (2b):



1b 2b



2b

The title compound was prepared according to the general procedure II, using 6,7-dichloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione **1b** (4.6 mg, 0.019 mmol) in xylene (0.3 ml), sprayed for 30 min. The crude product was subjected to flash column chromatography (100:0→95:05, EtOAc/Hexane), afforded the **2b** as a blue solid (2.1 mg, 62% yield). The spectroscopic data are consistent with the reported in the literature.[2]

Physical appearance: Yellow solid

Melting Point: 102-104 °C.

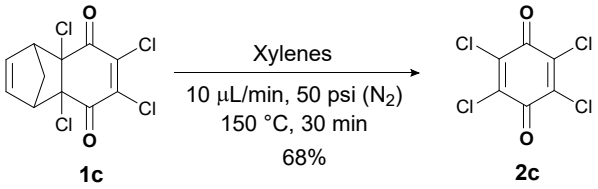
^{1}H NMR (500 MHz $CDCl_3$) δ ppm: 6.97 (s, 2H).

^{13}C NMR (125 MHz $CDCl_3$) δ ppm: 177.5, 141.4, 136.3.

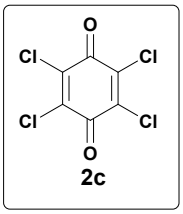
FT-IR (neat): 3065, 1676, 1562, 1289, 1245, 1106, 1042, 916, 840, 737 cm^{-1}.

HRMS: Calculated for $C_6H_2Cl_2O_2^-$ [M^-] 175.9437, found 175.9434.

2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione (2c):



1c 2c



2c

The title compound was prepared according to the general procedure II, using 4a,6,7,8a-tetrachloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione **1c** (5.9 mg, 0.019 mmol) in xylene (0.3 ml), sprayed for 30 min. The crude product was subjected to flash column chromatography (95:5→90:10, EtOAc/Hexane), afforded the **2c** as a blue solid (3.17 mg, 68% yield). The spectroscopic data are consistent with the reported in the literature.[3]

Physical appearance: Yellow solid

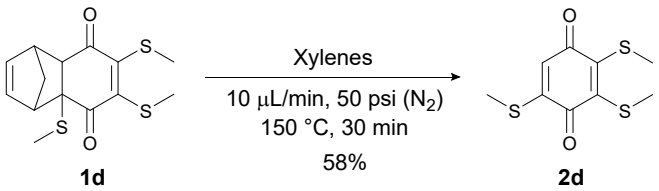
Melting Point: 287-289 °C.[4]

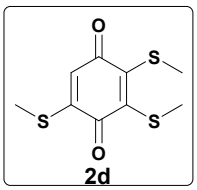
^{13}C NMR (DMSO-d6, 125 MHz) δ ppm: 169.7, 139.5.

FT-IR (neat): 1682, 1561, 1256, 1228, 1107, 904, 744, 707 cm^{-1}.

HRMS: Calculated for $C_6Cl_4O_2^-$ [M^-] 243.8658, found 243.8653.

2,3,5-tris(methylthio)cyclohexa-2,5-diene-1,4-dione (2d):





The title compound was prepared according to the general procedure II, using 4a,6,7-tris(methylthio)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione **1d** (5.9 mg, 0.019 mmol) in xylene (0.3 ml), sprayed for 30 min. The crude product was subjected to flash column chromatography (95:5→85:15, EtOAc/Hexane), and afforded the **2d** as a blue solid (2.7 mg, 58% yield). The spectroscopic data are consistent with the reported in the literature.[5]

Physical appearance: Blue solid.

Melting Point: 112-114 °C.

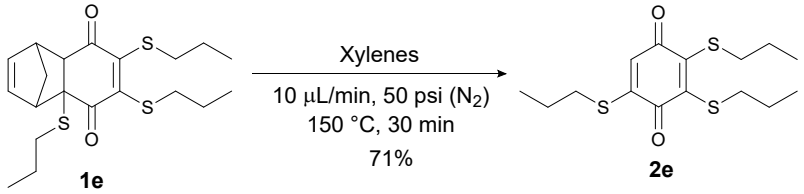
^{1}H NMR (500 MHz $CDCl_3$) δ ppm: 6.29 (s, 1H), 2.69 (s, 3H), 2.60 (s, 3H), 2.31 (s, 3H).

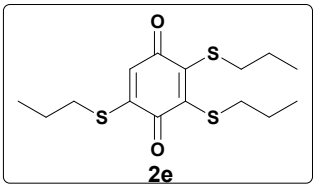
^{13}C NMR (125 MHz $CDCl_3$) δ ppm: 177.9, 177.3, 155.0, 148.1, 142.3, 125.5, 18.6, 18.1, 14.1.

FT-IR (neat): 2923, 1644, 1618, 1582, 1495, 1439, 1414, 1314, 1260, 1204, 1073, 978, 851, 785 cm^{-1}.

HRMS: Calculated for $C_9H_{11}O_2S_3^+$ [M+H$^+$] 246.9916, found 246.9916.

2,3,5-tris(propylthio)cyclohexa-2,5-diene-1,4-dione (2e):





The title compound was prepared according to the general procedure II, using 4a,6,7-tris(propylthio)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione **1e** (7.5 mg, 0.019 mmol) in xylene (0.3 ml) sprayed for 30 min. The crude product was subjected to flash column chromatography (95:5→90:10, EtOAc/Hexane), and afforded the **2e** as a blue solid (4.45 mg, 71% yield). The structure of the compound was confirmed by using ^{1}H NMR and ^{13}C NMR data.

Physical appearance: Dark blue liquid.

^{1}H NMR (500 MHz $CDCl_3$) δ ppm: 6.32 (s, 1H), 3.22 (t, *J* = 7.2 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.3 Hz, 2H), 1.76 (m, 2H), 1.63 (m, 4H), 1.07 (t, *J* = 7.4 Hz, 3H), 1.01 (m, 6H).

^{13}C NMR (125 MHz $CDCl_3$) δ ppm: 178.1, 177.5, 154.2, 148.5, 142.9, 125.6, 37.1, 36.7, 32.8, 24.0, 23.9, 21.1, 13.8, 13.5.

FT-IR (neat): 2363, 2926, 2870, 1634, 1582, 1486, 1458, 1389, 1261, 1236, 1194, 1069, 852, 780 cm^{-1}.

HRMS: Calculated for $C_{15}H_{23}O_2S_3^+$ [M+H$^+$] 331.0855, found 331.0857.

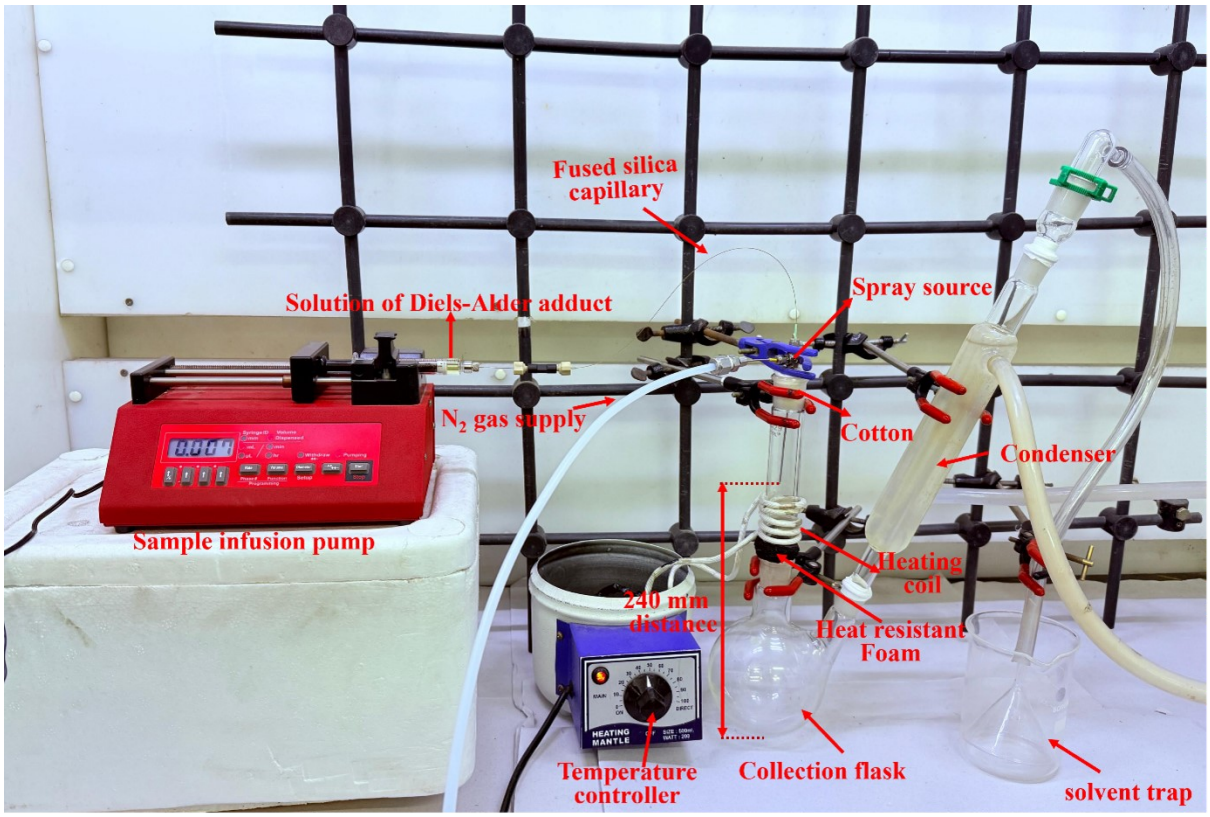
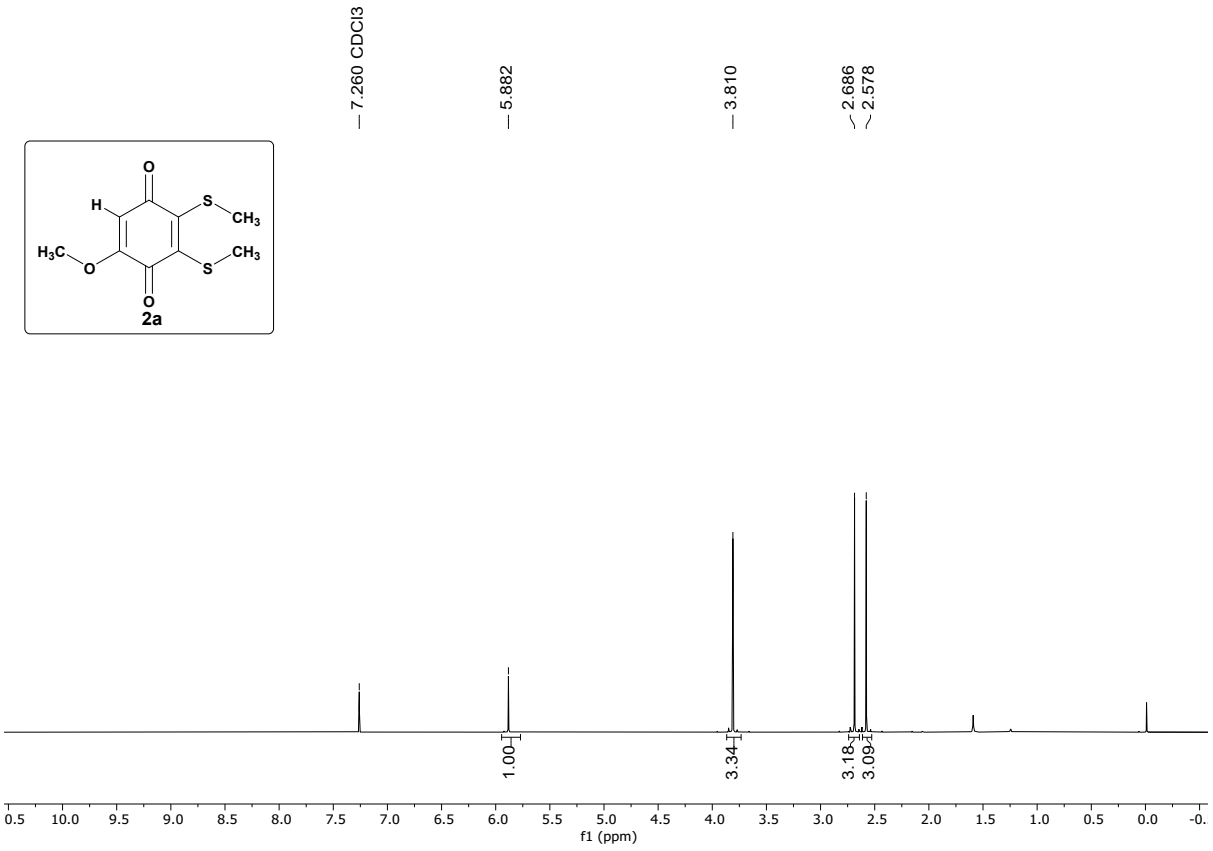
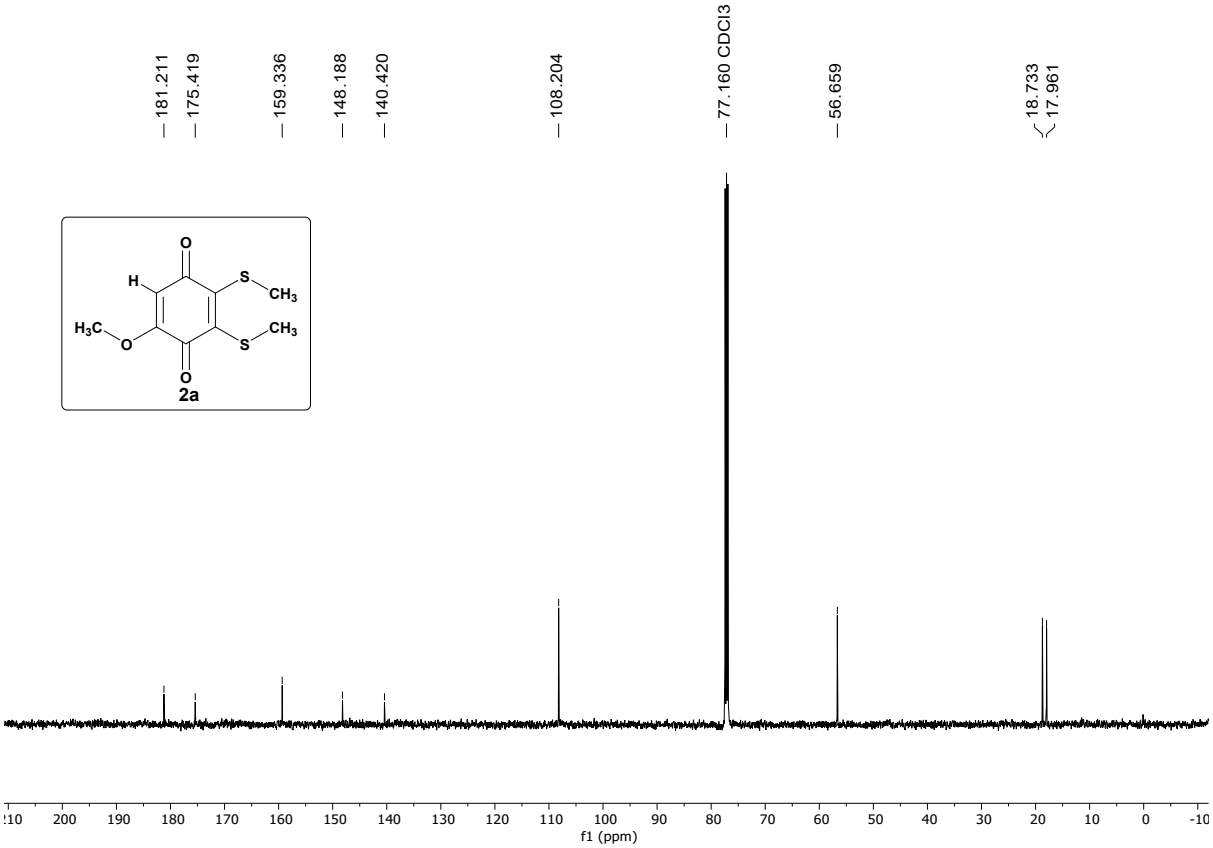
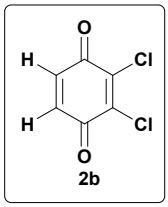


Figure S1: Experimental setup for the microdroplet-assisted retro-Diels-Alder reaction.

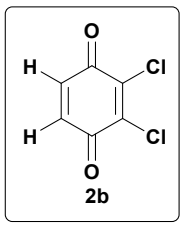
5. NMR Spectra of retro-Diels-Alder Product (2)



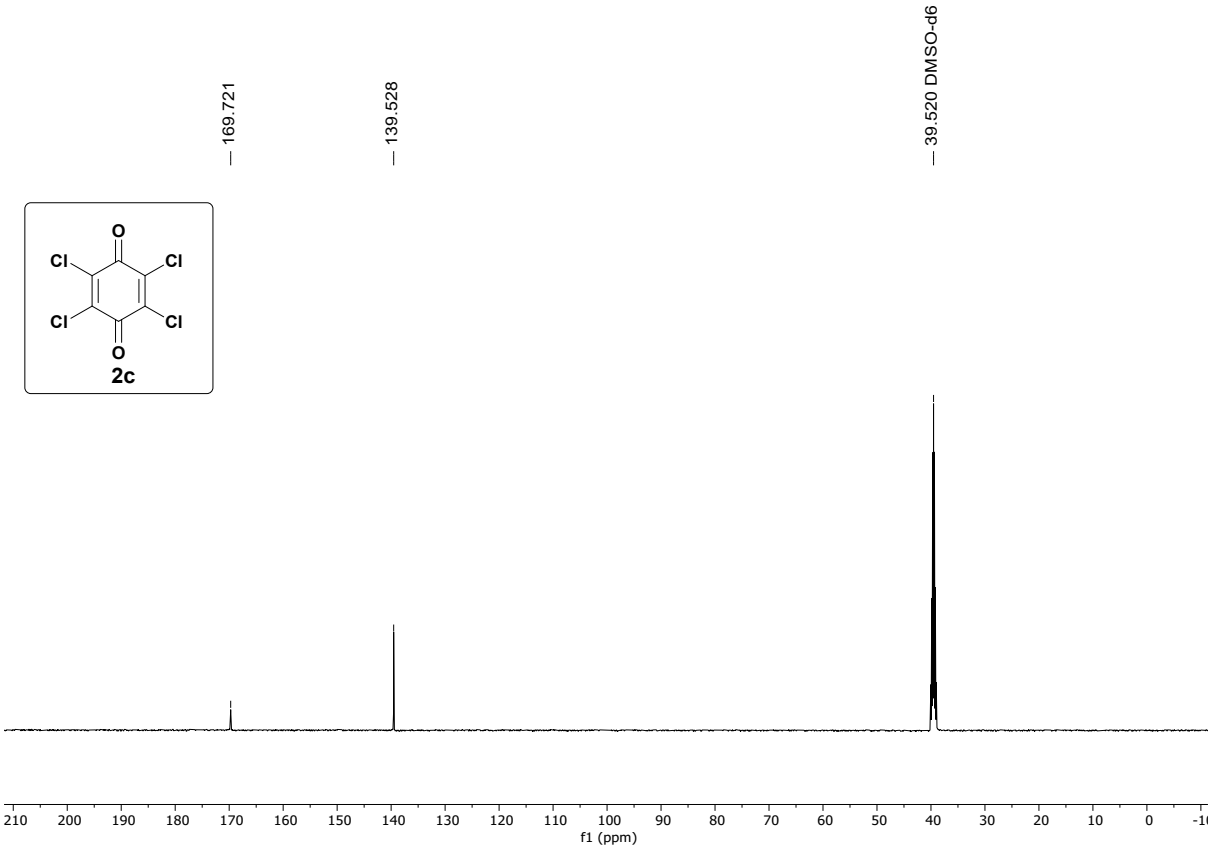


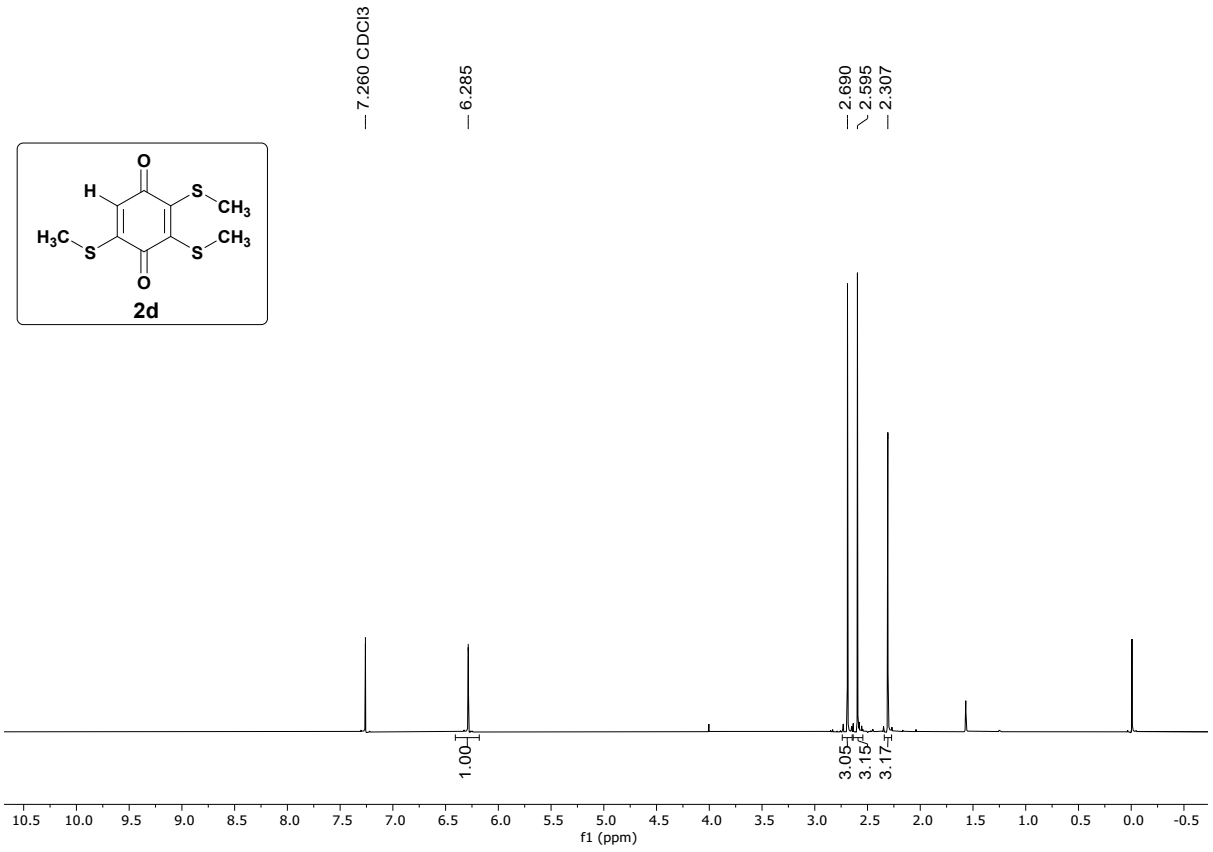

O
H
Cl
H
Cl
O
2b

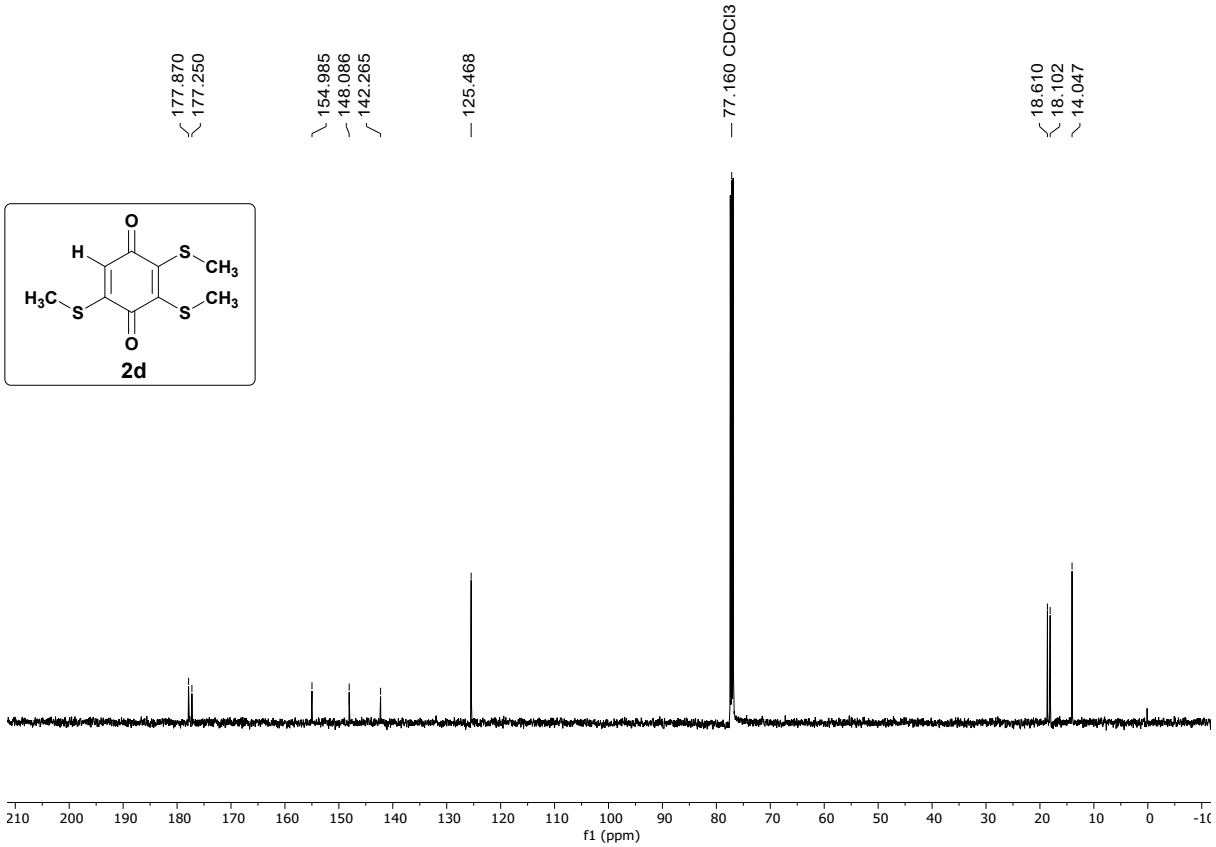
7.260 CDCl3
6.974
2.00
f1 (ppm)

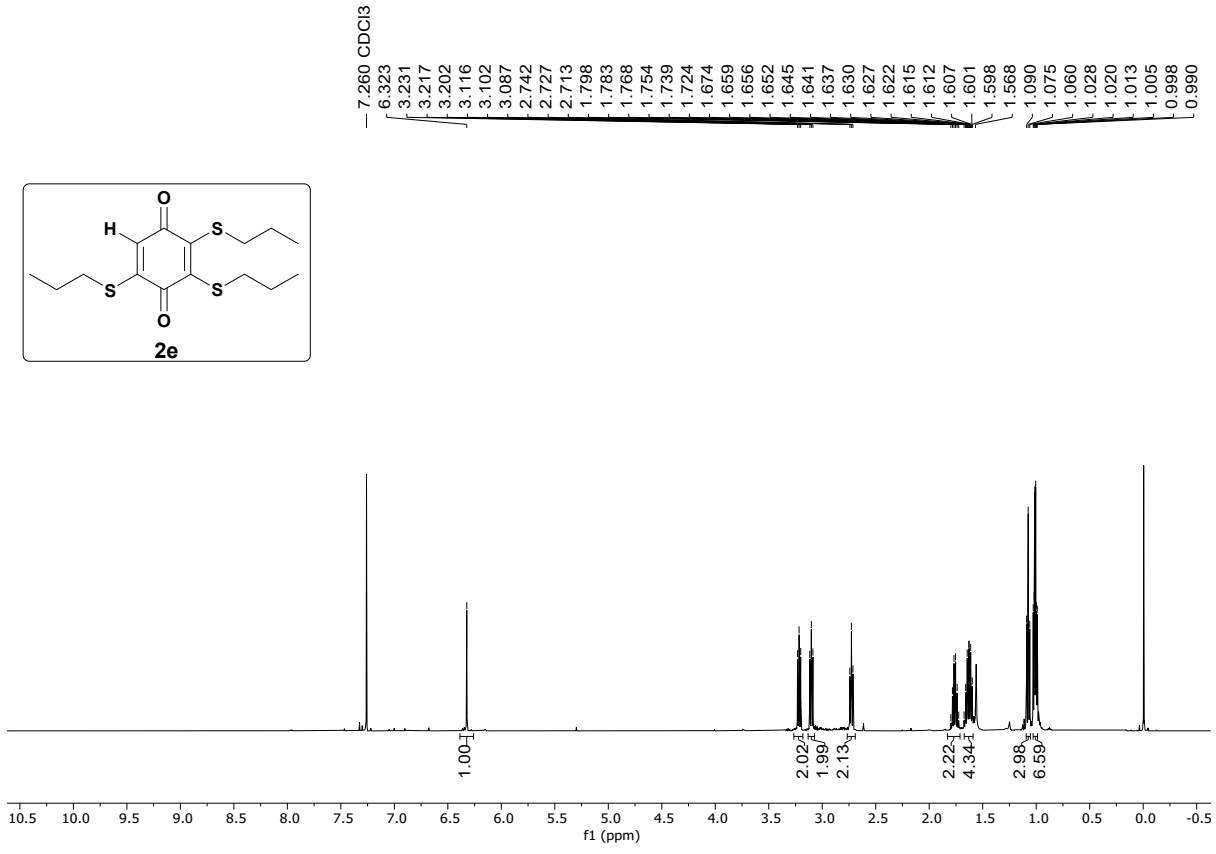

O
H
Cl
H
Cl
O
2b

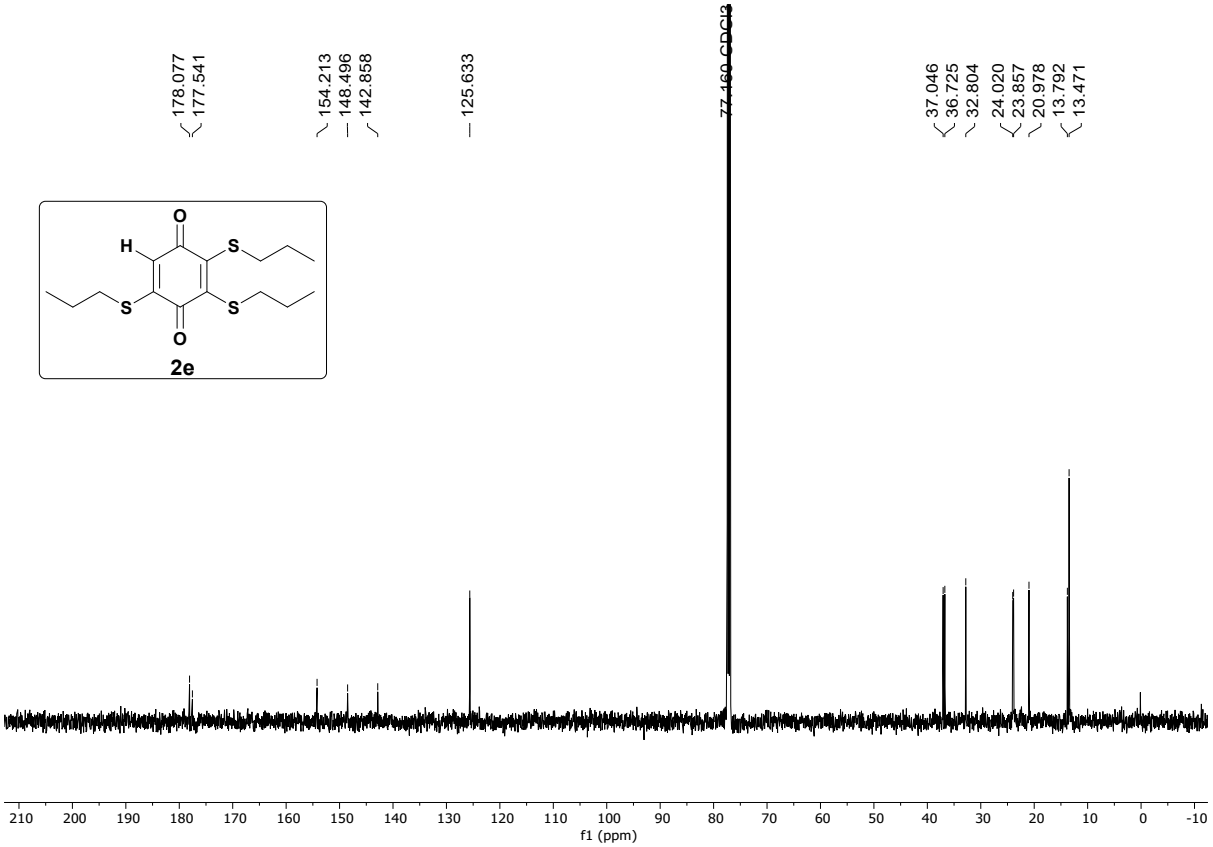
177.536
141.371
136.298
77.160 CDCl3
f1 (ppm)


169.721
139.528
39.520 DMSO-d6
O
Cl
Cl
Cl
Cl
O
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.260 CDCl3
6.285
2.690
2.595
2.307
O
H
S
CH3
H3C
S
S
CH3
O
2d
1.00
3.05
3.15
3.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

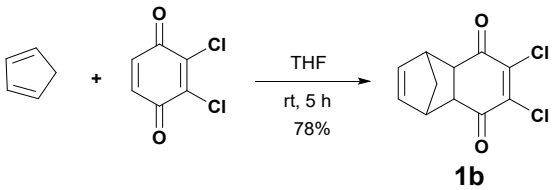

177.870
177.250
154.985
148.086
142.265
125.468
77.160 CDCl3
18.610
18.102
14.047
2d
f1 (ppm)


7.260 CDCl3
6.323
3.231
3.217
3.202
3.116
3.102
3.087
2.742
2.727
2.713
1.798
1.783
1.768
1.754
1.739
1.724
1.674
1.659
1.656
1.652
1.645
1.641
1.637
1.630
1.627
1.622
1.615
1.612
1.607
1.601
1.598
1.568
1.090
1.075
1.060
1.028
1.020
1.013
1.005
0.998
0.990
2e
1.00
2.02
1.99
2.13
2.22
4.34
2.98
6.59
f1 (ppm)



6. Synthesis of Starting Materials for retro-Diels-Alder reaction:

(i) Synthesis of 6,7-dichloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (1b)

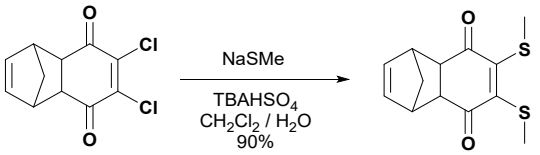


To a solution of 2,3-dichlorocyclohexa-2,5-diene-1,4-dione (0.354 g, 2 mmol) in 15 mL of THF was added to 2 mL of freshly distilled cyclopentadiene. After stirring for 5 h at room temperature, the solution was concentrated under reduced pressure. The resultant solid was washed with cold hexane and dried in vacuum which afforded **1b** as off white solid (0.380 g, 78%). The spectroscopic data are consistent with the reported in the literature.[1,6]

^{1}H NMR (500 MHz $CDCl_3$) δ ppm: 6.10 (t, *J* = 1.8 Hz, 2H), 3.62 (m, 2H), 3.43 (dd, *J* = 2.5, 1.4 Hz, 2H), 1.59 (m, 1H), 1.50 (m,1H)

^{13}C NMR (125 MHz $CDCl_3$) δ ppm: 189.0, 147.4, 135.6, 49.6, 49.1, 48.7.

(ii) Synthesis of 6,7-bis(methylthio)-1,4,4a,8a-tetrahydro-1,4-methano-naphthalene-5,8-dione

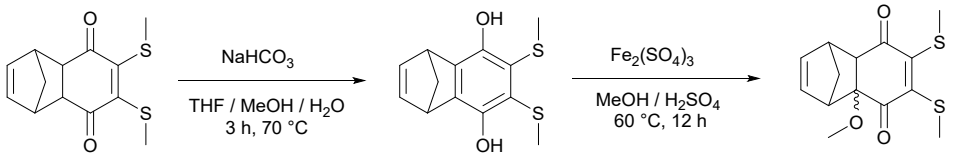


6,7-dichloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (0.365 g, 1.5 mmol, 1 equiv.) was dissolved in 20 mL of CH_2Cl_2 and transferred to a separatory funnel. 20 mL of an aqueous solution containing NaSMe (0.21 g, 3 mmol, 2 equiv.) and tetrabutylammonium hydrogensulfate (0.031 g, 0.09 mmol, 0.06 equiv.) were added to the separatory funnel. The funnel was capped and shaken for approximately two minutes. The phases were separated, and the organic layer was collected. The aqueous fraction was extracted with an additional 20 mL of CH_2Cl_2. The organic fractions were pooled, dried with Na_2SO_4, and concentrated under reduced pressure to afford 6,7-bis(methylthio)-1,4,4a,8a-tetrahydro-1,4-methano-naphthalene-5,8-dione as yellow solid (0.359 g, 90%). The spectroscopic data are consistent with the reported in the literature.[1,6]

^{1}H NMR (500 MHz $CDCl_3$) δ ppm: 6.09 (t, *J* = 1.9 Hz, 2H), 3.45 (m, 2H), 3.33 (m, 2H), 2.46 (s, 6H), 1.56 (m, 1H), 1.41 (m, 1H).

^{13}C NMR (125 MHz $CDCl_3$) δ ppm: 191.6, 150.4, 136.3, 50.6, 48.3, 46.9, 16.9.

(iii) Synthesis of 4a-methoxy-6,7-bis(methylthio)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (1a)



1a

Overall yield : 65%

6,7-bis(methylthio)-1,4,4a,8a-tetrahydro-1,4-methano-naphthalene-5,8-dione (400 mg, 1.5 mmol, 1equiv.) was dissolved in a 1:1:1 mixture of THF, MeOH, and H_2O (6:6:6 ml), and 5 equivalents of $NaHCO_3$ (60 mg, 7.5 mmol, 5 equiv.) were added to this solution. The resulting mixture was heated at 70°C for 3 h. After cooling to room temperature, the suspension was acidified with 1M HCl and transferred to a separatory funnel with 20 mL of H_2O and 30 mL of CH_2Cl_2. The layers were separated, and the organic fraction was collected. The aqueous fraction was extracted with 1 × 20 mL of CH_2Cl_2 and 1 × 20 mL of EtOAc. The organic extracts were pooled, dried with Na_2SO_4, and concentrated under reduced pressure.

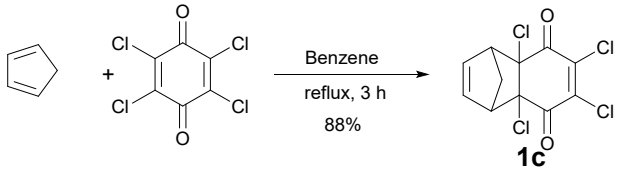
Further the resulting mixture was dissolved in a mixture was dissolved in a mixture of MeOH (35 mL) and H_2SO_4 (1 mL), $Fe_2(SO_4)_3$ (900 mg, 2.25 mmol, 1.5 equiv.) was added, and the

resulting suspension was heated to 60 °C for 12 h. the color of the suspension first became dark red and then transitioned to dark yellow over this period. After cooling to room temperature, this solution was transferred to a separatory funnel with 50 mL of H_2O and 50 mL of CH_2Cl_2. The layers were separated, and the aqueous fraction was extracted with 2 x 20 mL of CH_2Cl_2. The organic fractions were combined, dried with Na_2SO_4, and concentrated under reduced pressure. Further the crude reaction mixture purified through column chromatography, which afforded the **1a** as yellow solid (0.288g, 65%) with mixture of diastereomers (75:25). The spectroscopic data are consistent with the reported in the literature.[1]

^{1}H NMR (500 MHz $CDCl_3$) δ ppm: 6.24 (dd, *J* = 5.7, 2.9 Hz, 1H), 5.91 (dd, *J* = 5.7, 3.3 Hz, 1H), 3.44 (m, 1H), 3.35 (m, 1H), 3.31 (s, 3H), 3.05 (d, *J* = 3.7 Hz, 1H), 2.48 (s, 3H), 2.46 (s, 3H), 1.84 (dt, *J* = 8.8, 1.6 Hz, 1H), 1.68 (dt, *J* = 8.8, 1.8 Hz, 1H).

^{13}C NMR (125 MHz $CDCl_3$) δ ppm: 190.3, 187.3, 150.3, 149.2, 140.3, 134.8, 87.3, 61.6, 52.5, 45.6, 45.1, 44.2, 16.7, 16.5.

(iv) Synthesis of 4a,6,7,8a-tetrachloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (1c)

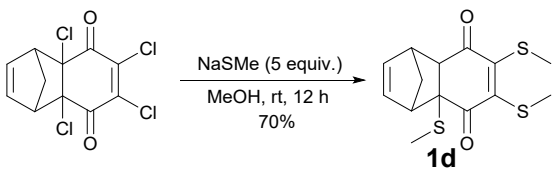


To a solution of tetrachloro-1,4-benzoquinone (1.97 g, 8 mmol) in 20 mL of benzene was added to 2 mL of freshly distilled cyclopentadiene. After stirring for 3 h at reflux, the solution was concentrated under reduced pressure. The resultant solid was washed with cold hexane and dried in the vacuum to afford **1c** as off-white solid (2.2 g, 88 %). The spectroscopic data are consistent with the reported in the literature. [7]

^{1}HNMR(400 MHz, $CDCl_3$) δ ppm: 6.16 (s, 2H), 3.64 (m, 2H), 2.47 (dt, *J* = 10.3, 1.6 Hz, 1H), 2.07 (dt, *J* = 10.3, 1.7 Hz, 1H).

^{13}C NMR (124 MHz, $CDCl_3$) δ ppm: 181.3, 145.2, 138.3, 74.8, 54.8, 45.0.

(v) Synthesis of 4a,6,7-tris(methylthio)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (1d)

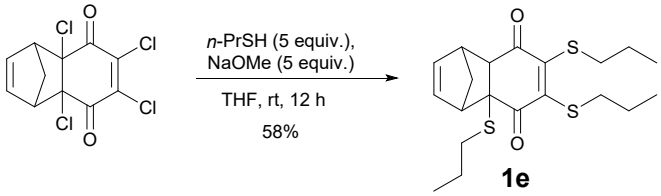


To a solution of 4a,6,7,8a-tetrachloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione 3 (0.47 g, 1.5 mmol, 1 equiv.) in MeOH (10 mL) was added NaSMe (0.52 g, 7.5 mmol, 5 equiv.). The resulting reaction mixture was stirred at room temperature for 12 h. The excess solvent was evaporated in vacuum, the reaction was quenched with saturated NH_4CI solution (20 mL) and extracted with EtOAc (3×30 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified through column chromatography (95:05 → 90:10 hexane/EtOAc), afforded **1d** as yellow solid (330 mg, 70%). The spectroscopic data are consistent with the reported in the literature. [5]

^{1}HNMR(400 MHz, $CDCl_3$) δ ppm: 6.18 (dd, *J* = 5.6, 2.9 Hz, 1H), 6.09 (dd, *J* = 5.6, 3.1 Hz, 1H), 3.49 (m, 1H), 3.34 (m, 1H), 2.94 (d, *J* = 3.8 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H), 2.11 (s, 3H), 2.04 (m, 1H), 1.63 (dt, *J* = 9.1, 1.9 Hz, 1H).

^{13}C NMR (124 MHz, $CDCl_3$) δ ppm: 189.2, 182.7, 152.7, 145.1, 138.4, 137.2, 60.3, 59.4, 45.8, 45.8, 44.9, 16.5, 16.0, 13.2.

(vi) Synthesis of 4a,6,7-tris(propylthio)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (1e)

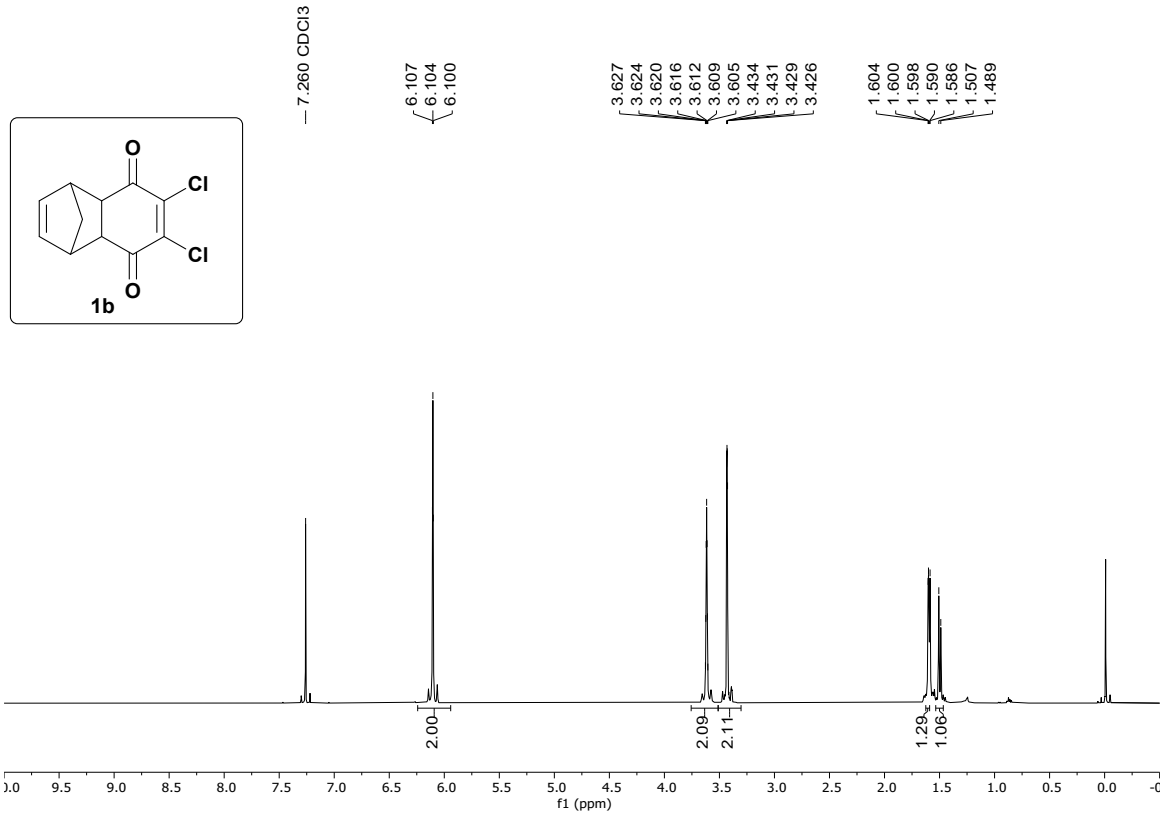


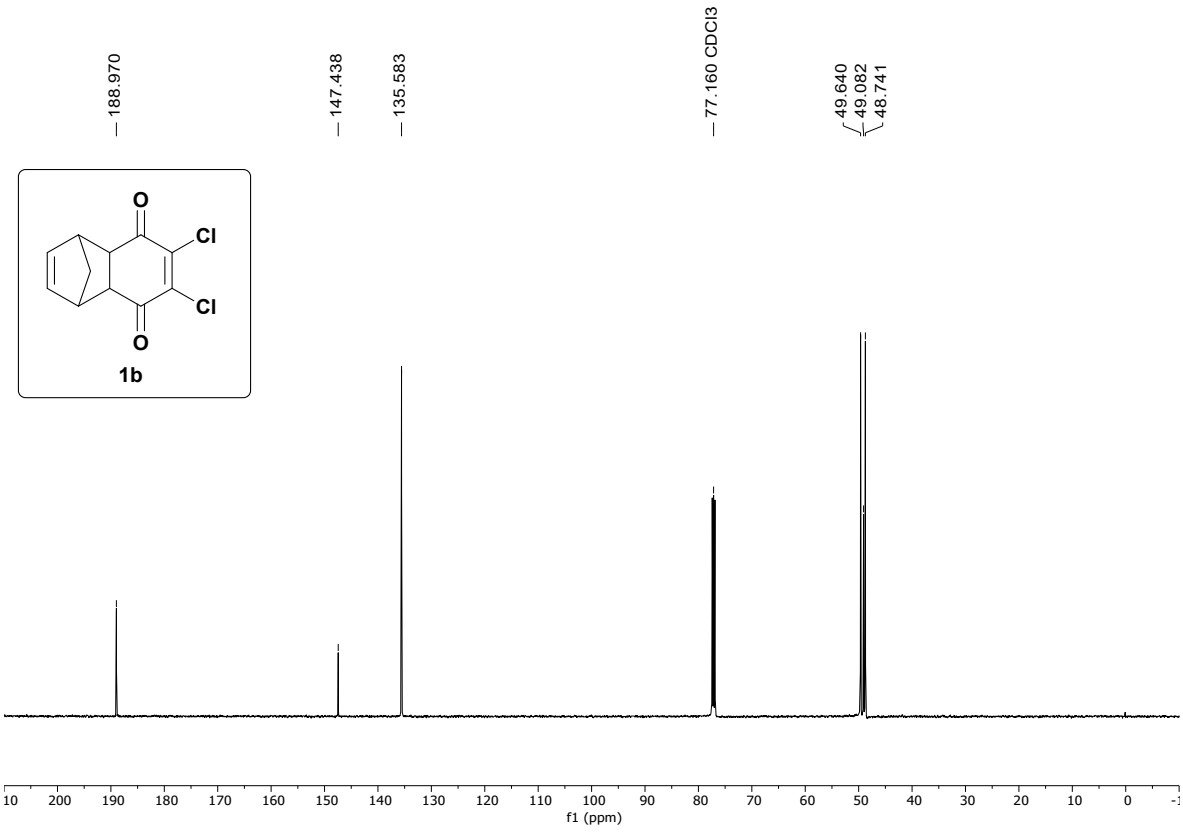
To a solution of 4a,6,7,8a-tetrachloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (0.47 g, 1.5 mmol, 1 equiv.) in THF (15 mL) was added propane thiol (0.57 g, 7.5 mmol, 5 equiv.). NaOMe (0.4 g, 7.5 mmol, 5 equiv.) was added, and the reaction was stirred for 12 hours at room temperature. The excess solvent was evaporated in vacuum, the reaction was quenched with saturated NH_4CI solution (20 mL) and extracted with EtOAc (3×30 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product. Further the crude compound was purified through column chromatography (98:02 → 95:05 hexane/EtOAc), afforded **1e**, as yellow solid (345 mg, 58%). The structure of the compound was confirmed by using ^{1}H NMR and ^{13}C NMR data.

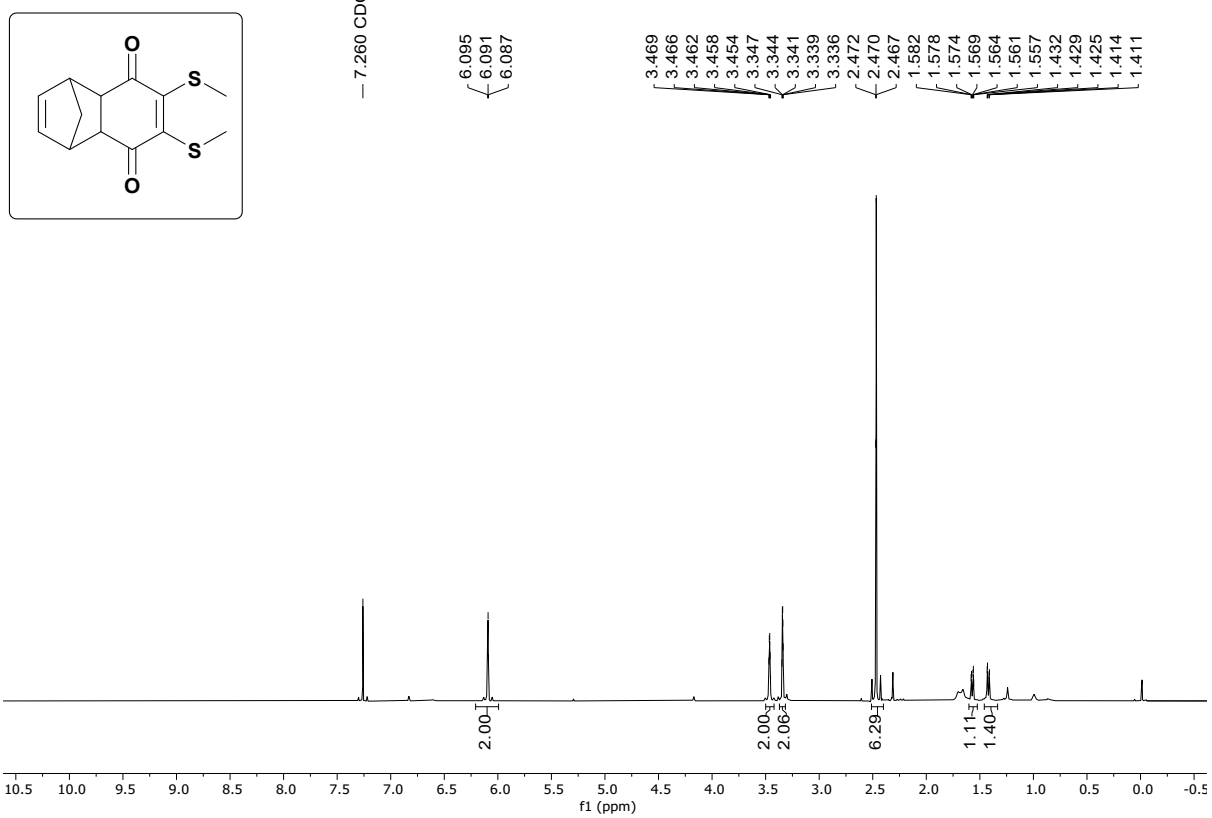
^{1}HNMR(400 MHz, $CDCl_3$) δ ppm: 6.15 (dd, *J* = 5.6, 2.9 Hz, 1H), 6.08 (dd, *J* = 5.6, 3.0 Hz, 1H), 3.48 (m, 1H), 3.35 (m, 1H), 2.96 (m, 6H), 2.74 (m, 1H), 2.41 (m, 1H), 2.08 (dd, *J* = 9.0, 1.5 Hz, 1H), 1.62 (m, 6H), 1.00 (m, 9H).

^{13}C NMR (124 MHz, $CDCl_3$) δ ppm: 189.7, 184.2, 152.8, 145.7, 138.3, 137.4, 60.6, 59.3, 47.1, 45.8, 44.9, 35.1, 35.0, 32.2, 24.0, 23.7, 22.5, 13.9, 13.6, 13.4.

7. NMR Spectra of starting materials:



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6.087
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3.347
3.344
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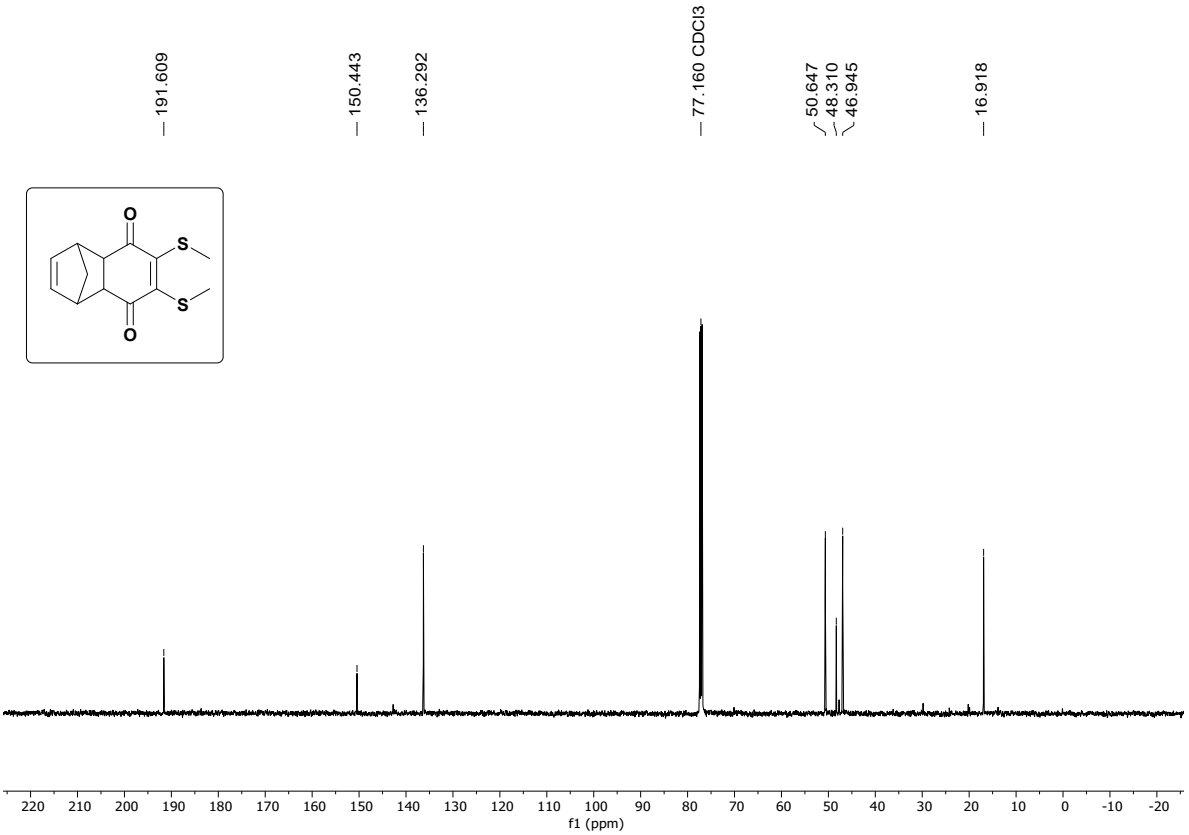
3.339
3.336
2.472
2.470
2.467
1.582
1.578
1.574
1.569
1.564
1.561
1.557
1.432
1.429
1.425
1.414
1.411
2.00
2.00
2.06
6.29
1.11
1.40
f1 (ppm)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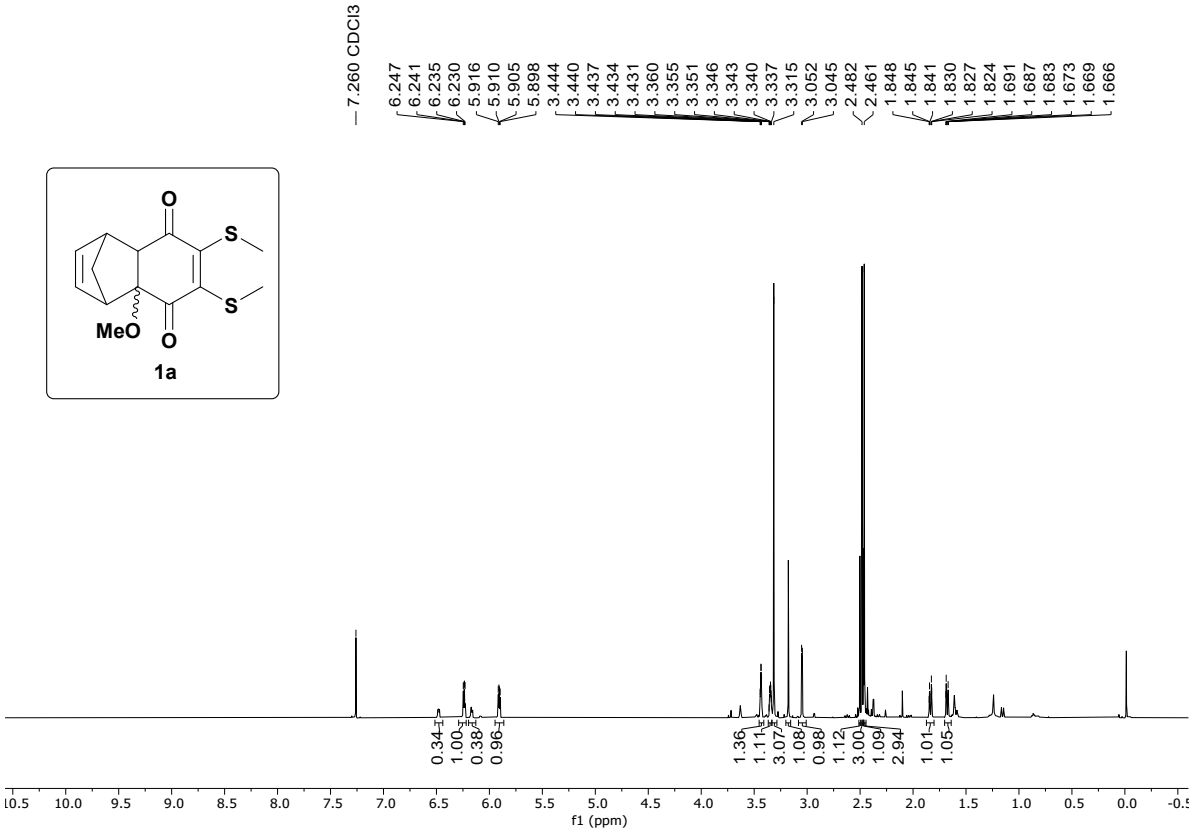
48.310
46.945
16.918
f1 (ppm)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6.235
6.230
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5.905
5.898
3.444
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3.434
3.431
3.360
3.355
3.351
3.346
3.343
3.340
3.337
3.315
3.052
3.045
2.482
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1.845
1.841
1.830
1.827
1.824
1.691
1.687
1.683
1.673
1.669
1.666
O
S
S
MeO
O
1a
0.34
1.00
0.38
0.96
1.36
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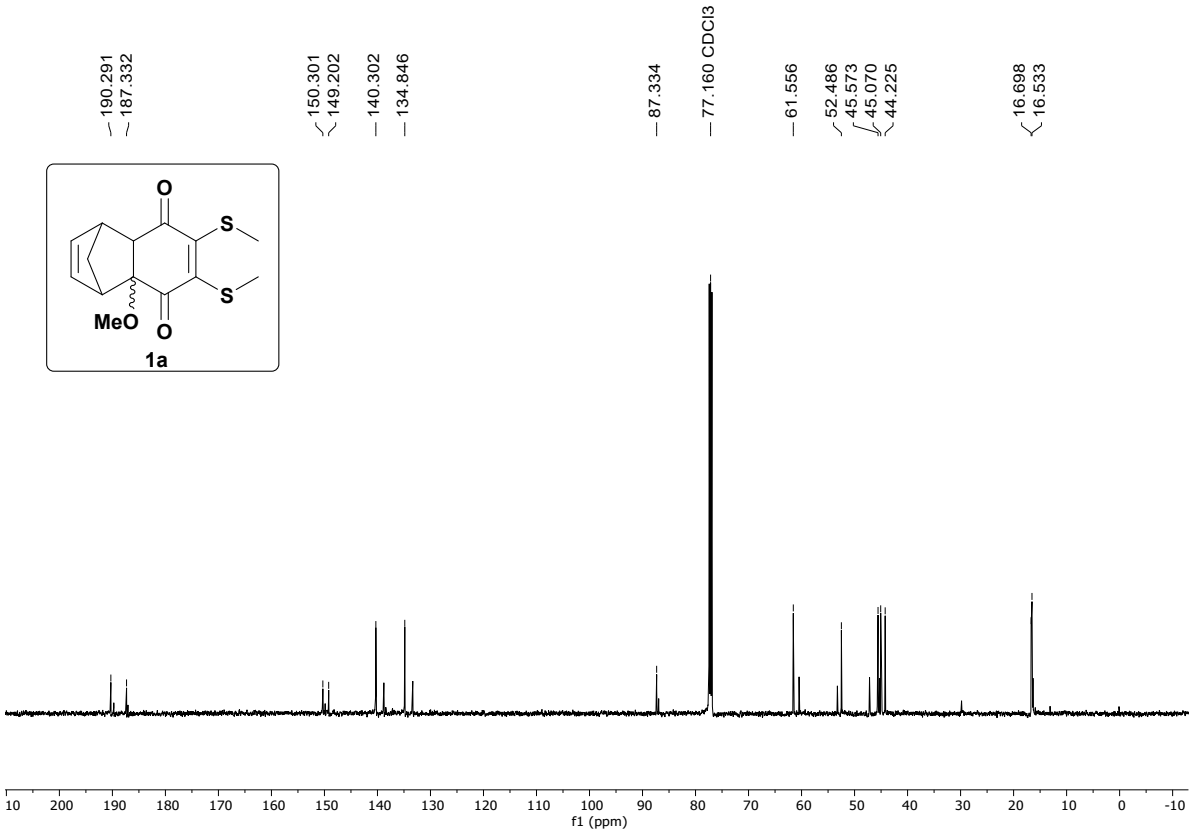
1.12
3.00
1.09
2.94
1.01
1.05
f1 (ppm)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140.302
134.846
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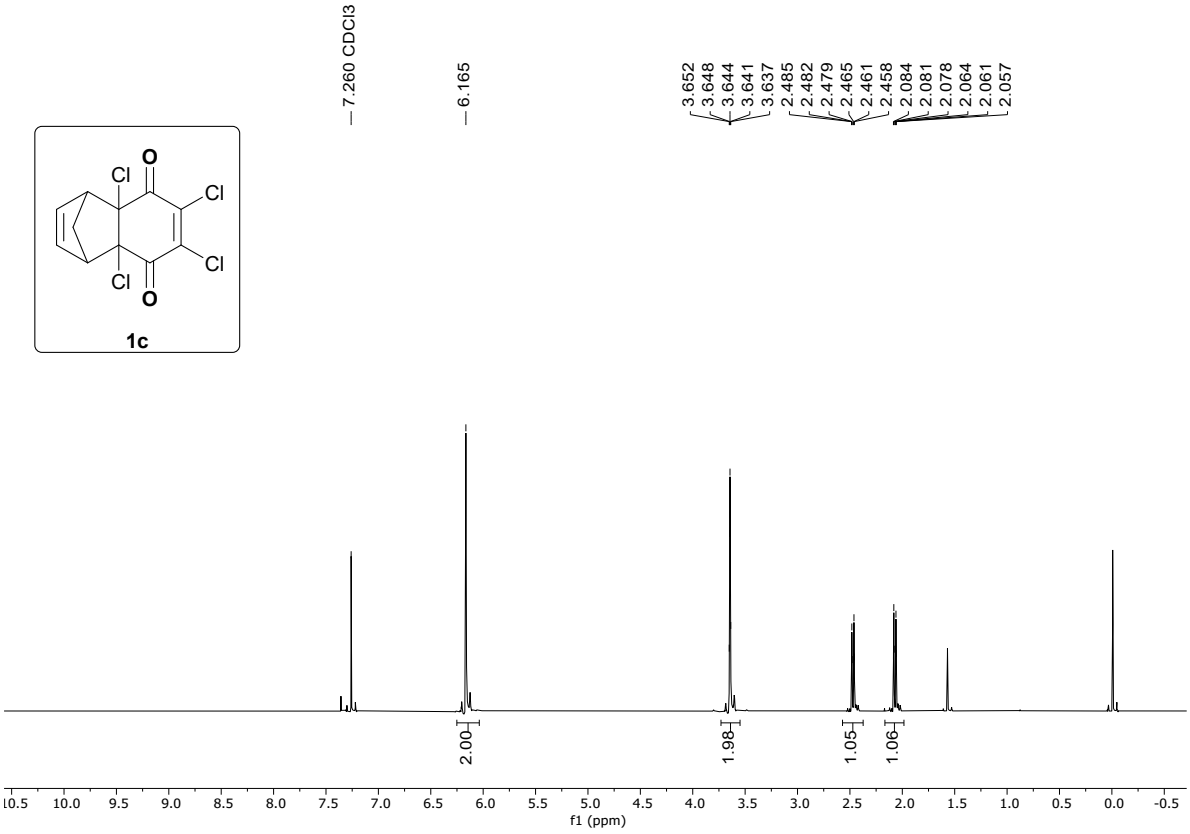
45.070
44.225
16.698
16.533
O
S
S
MeO
O
1a
f1 (ppm)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3.644
3.641
3.637
2.485
2.482
2.479
2.465
2.461
2.458
2.084
2.081
2.078
2.064
2.061
2.057
Cl
O
Cl
Cl
Cl
O
1c
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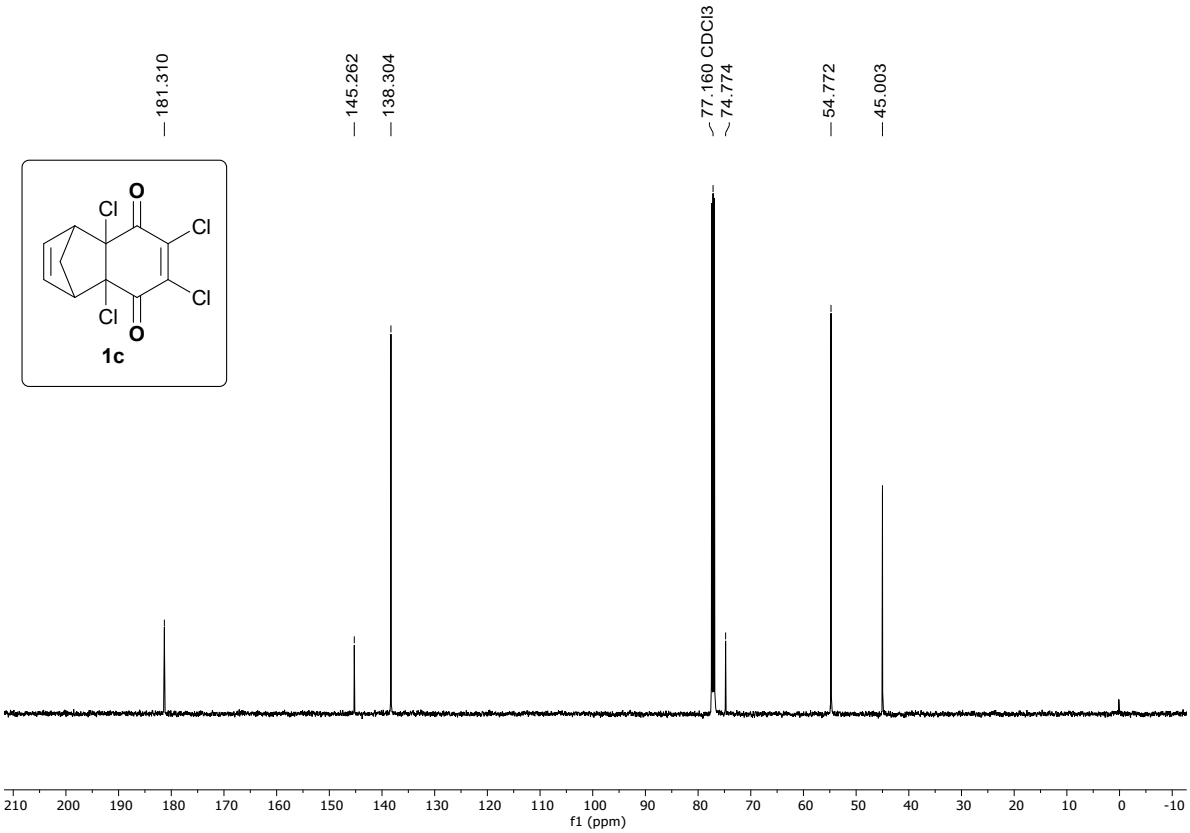
1.98
1.05
1.06
f1 (ppm)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Cl
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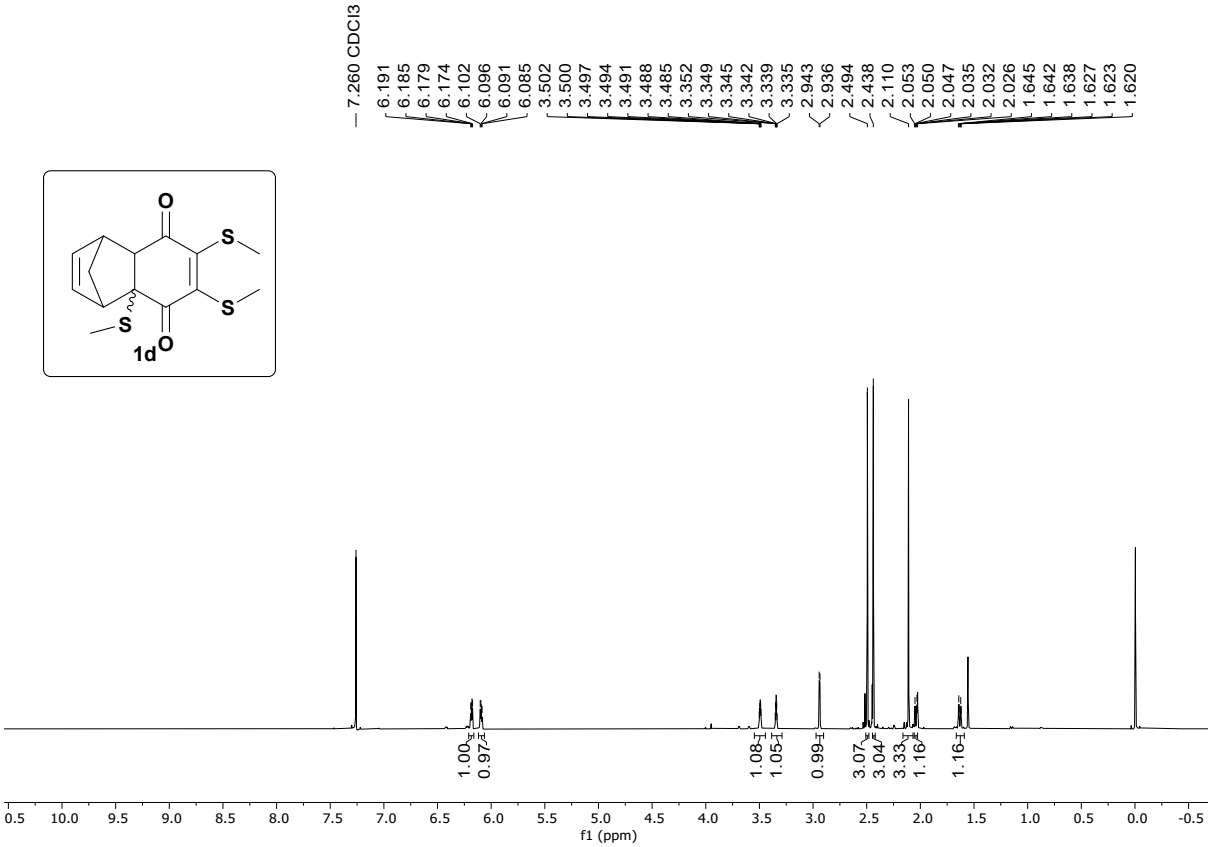
Cl
Cl
Cl
O
1c
f1 (ppm)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6.174
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6.091
6.085
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3.500
3.497
3.494
3.491
3.488
3.485
3.352
3.349
3.345
3.342
3.339
3.335
2.943
2.936
2.494
2.438
2.110
2.053
2.050
2.047
2.035
2.032
2.026
1.645
1.642
1.638
1.627
1.623
1.620
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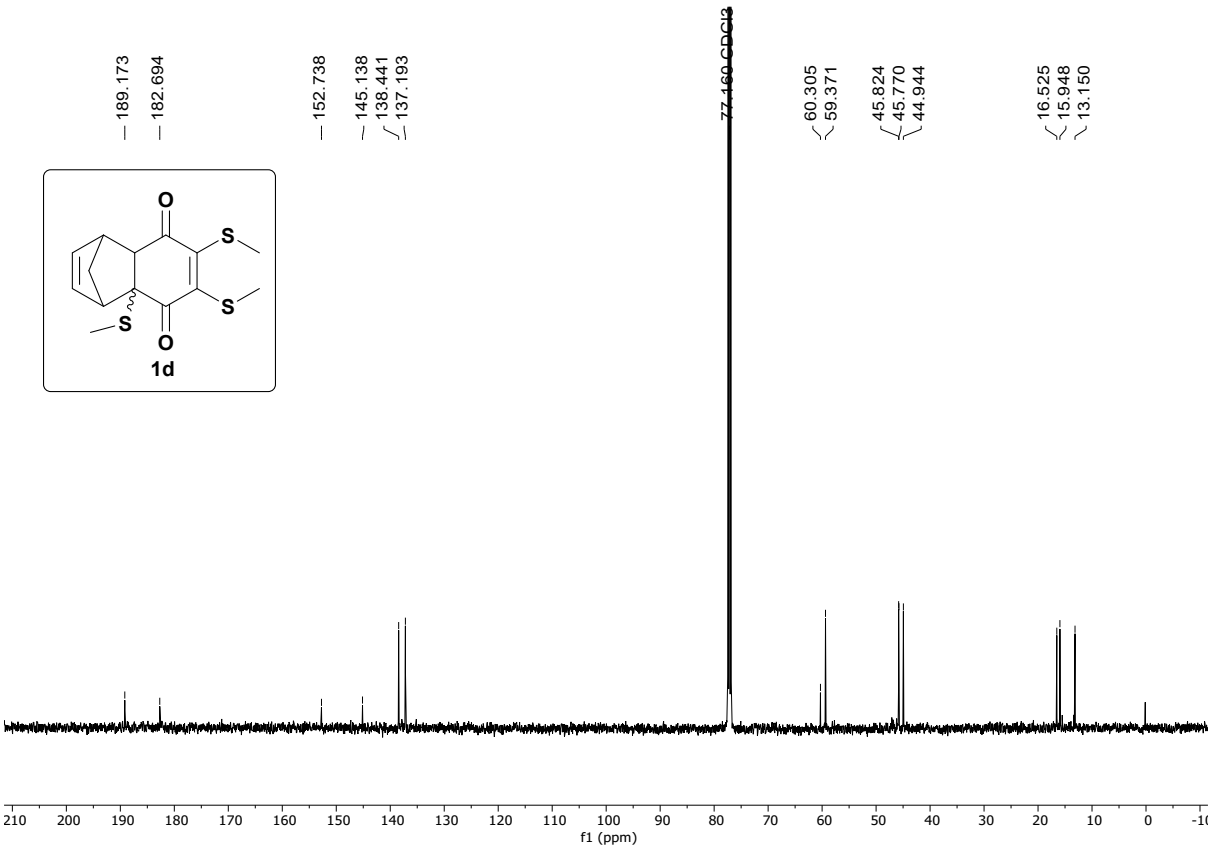
1.00
0.97
1.08
1.05
0.99
3.07
3.04
3.33
1.16
1.16
f1 (ppm)


189.173
182.694
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138.441
137.193
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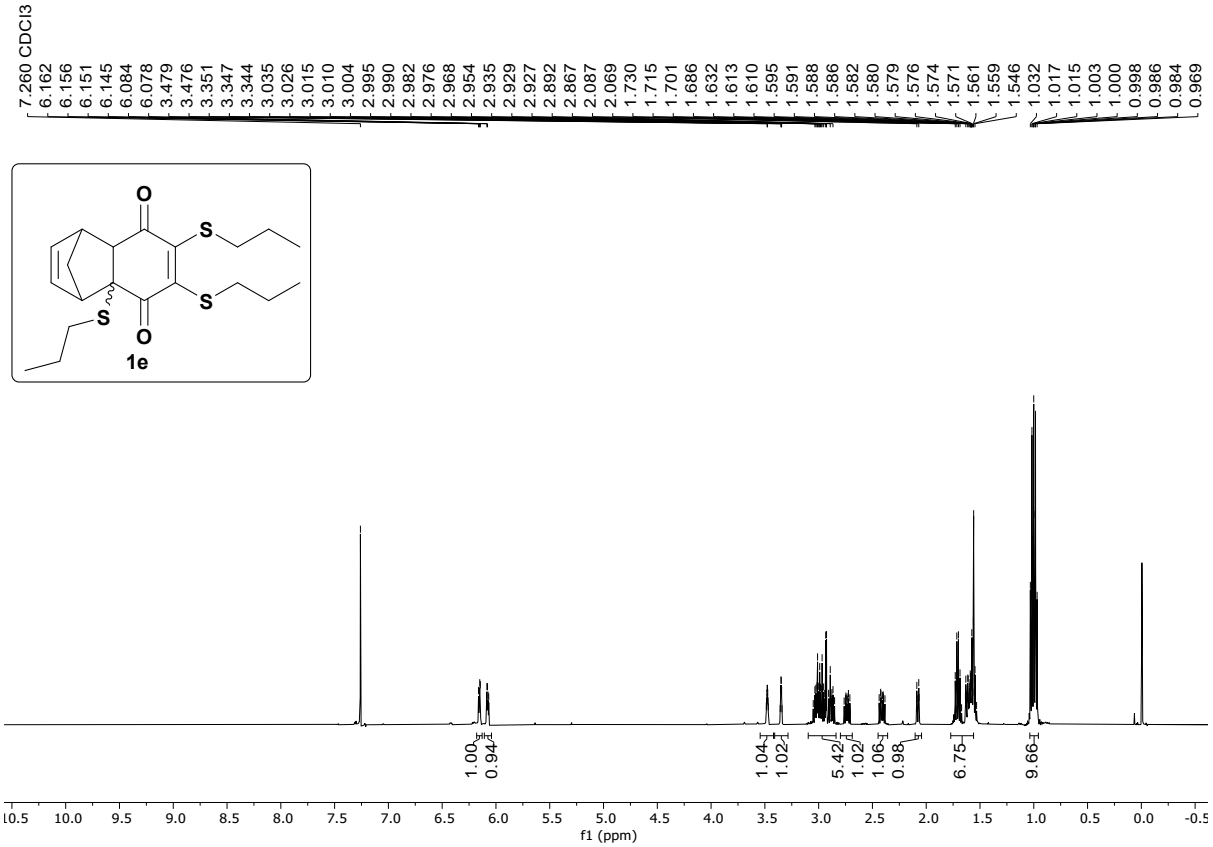
16.525
15.948
13.150
1d
f1 (ppm)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6.151
6.145
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3.347
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2.968
2.954
2.935
2.929
2.927
2.892
2.867
2.087
2.069
1.730
1.715
1.701
1.686
1.632
1.613
1.610
1.595
1.591
1.588
1.586
1.582
1.580
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1.571
1.561
1.559
1.546
1.032
1.017
1.015
1.003
1.000
0.998
0.986
0.984
0.969
O
S
S
S
O
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1.00
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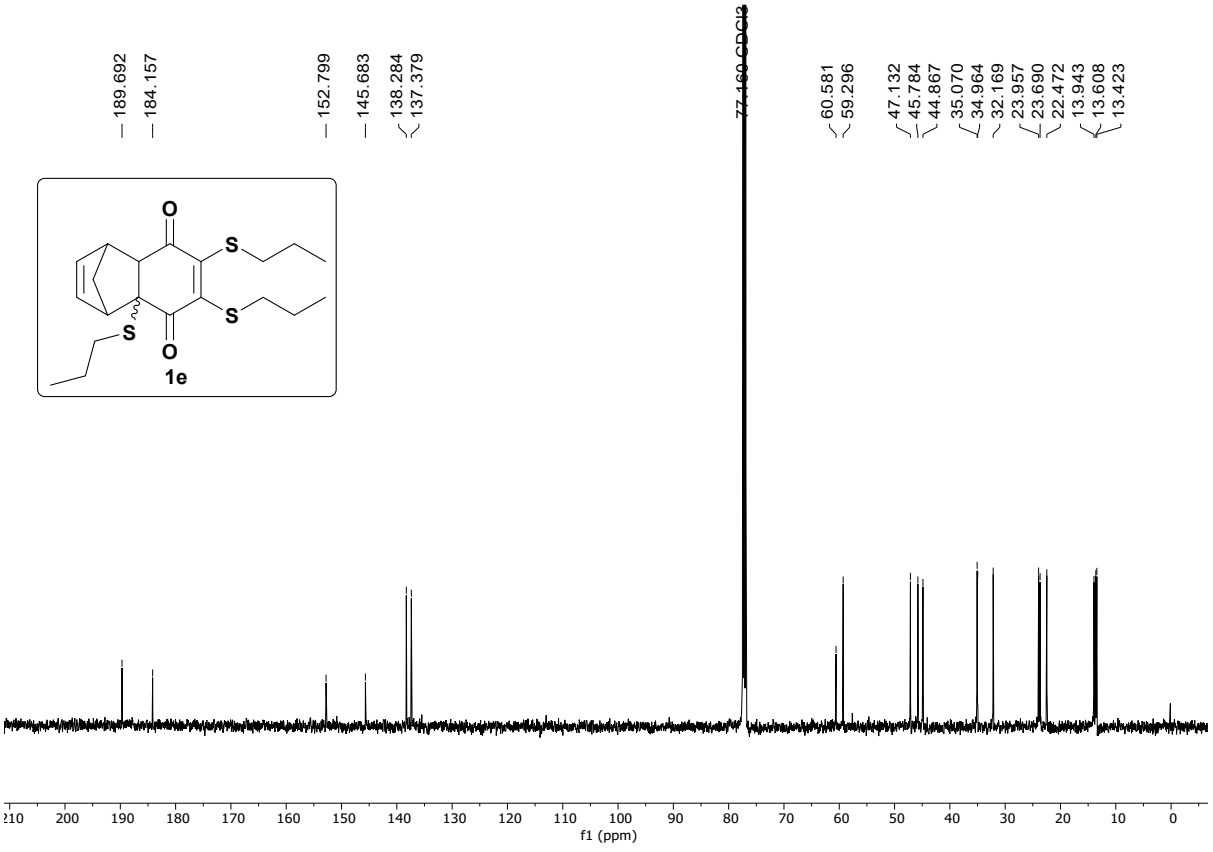
5.42
1.02
1.06
0.98
6.75
9.66
f1 (ppm)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44.867
35.070
34.964
32.169
23.957
23.690
22.472
13.943
13.608
13.423
O
S
S
S
O
1e
f1 (ppm)

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